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### AN OVERVIEW OF PROCESS OPTIONS AND BEHAVIORAL ASPECTS OF THE COPPER VALUES RECOVERED FROM THE COPPER BLEED STREAM OF A COPPER SMELTER DEVELOPED AT THE NATIONAL METALLURGICAL LABORATORY

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## **AN OVERVIEW OF PROCESS OPTIONS AND BEHAVIORAL ASPECTS OF THE COPPER VALUES RECOVERED FROM THE COPPER BLEED STREAM OF A COPPER SMELTER DEVELOPED AT THE NATIONAL METALLURGICAL LABORATORY**

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In the present research, an effort has been made to prepare copper salt/powder from the copper bleed stream generated during the electrowinning of pure copper from the copper anode in a copper smelter. Various approaches have been opted for the complete recovery of copper values such as: evaporation–crystallization, electrolytic process, and direct hydrogen reduction. Physical and chemical properties of copper powder/salt produced from the large-scale experiments from actual plant and model solutions have been evaluated for P/M applications and compared with the standard properties. Thus, mixed crystal suitable for recycling back to the system as a makeup salt containing nickel in a tolerable range could be recovered by evaporation and crystallization of the bleed stream up, to 50%. Copper powder recovery by the electrolysis process at a current density of  $700 \text{ A/m}^2$  was about 95%. Scanning electron microscope examination showed that the powder was dendritic in nature. On annealing, the purity of the copper powder was found to be 99.95%. The annealed powder had apparent density of  $3.04 \text{ g/cc}$ , hydrogen loss 0.72%, and acid insoluble as 0.27%. On compaction of  $<104\text{-}\mu\text{m}$  sized powder, the green density was found to be  $8.7 \text{ g/cc}$ . Similarly, the recovery of the copper powder obtained

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from the model copper solution by the hydrogen reduction process was found to be >99% and the annealed powder had an apparent density of 3.50 g/cc, flow rate 35.6 g/min, hydrogen loss 0.195%, purity 99.8%, and green density of 8.57 g/cc while the powder from the actual plant solution was found to have an apparent density of 3.49 g/cc, flow rate 46.0 g/min, hydrogen loss 0.598%, purity 99.4%, and green density 8.57 g/cc for the powder <100 µm in size. Thus, the properties of copper powder produced by hydrogen reduction and electrolytic route were compared and were found to be suitable for the P/M applications.

**Keywords:** copper powder, crystallization, electrolysis, hydrogen reduction, powder properties

## 1. INTRODUCTION

The recycling and reuse of industrial waste is now the major weapon for environmentalists to combat strict environmental rules, thus making wealth out of waste vis a vis environmental protection. Since industrial wastes/byproducts are rich in metals such as copper, nickel, zinc, lead, etc., they are thus considered to be secondary raw materials for the recovery of these metals as their salts/powders as desired. Copper bleed stream (CBS) is one such spent stream, which is generated during the purification of impure copper in the electrefining plant containing 40–50 g/L Cu, 170–200 g/L H<sub>2</sub>SO<sub>4</sub>, 20 g/L Ni, 1–2 g/L Fe, and traces of other impurities such as As, Sb, Bi, Cl, etc. During the course of the investigation, the following studies were carried out to optimize the parameters for the recovery of value added product viz metal powders/their salts, besides the acid that could be recycled back to the system.

- 1) Synthesis of copper sulphate from CBS by evaporative crystallization.
- 2) Synthesis of electrolytic grade copper powder following Partial decopperization–crystallization–solvent extraction–electro winning of the pure copper solution route.
- 3) Synthesis of pure copper powder by direct hydrogen reduction of CBS.

This article details all the process steps opted for the recovery of copper values from the CBS from a copper smelter. Work done by other authors on the various processes opted in this work, as cited in the literature, are briefly discussed here.

*Crystallization:* For producing value-added products from waste streams like CBS, various separation processes such as crystallization, solvent extraction, and precipitation could be considered. Crystallization (Jancic and Grootsholten 1984; Mersmann et al. 1994; Mullin 1997; Myerson 1993) is an established industrial process and is often critical because it largely determines product purity and handling characteristics such as caking, wetting, or losses due to dusting. In many cases, the process is employed as an energetically advantageous way to separate an individual compound from a mixture of substances represented by raw materials or byproducts of a reaction. A numbers of critical reviews (Nývlt et al. 1985; Söhnel and Garside 1992; Tavare 1995; Buckley 1952; Strickland-Constable 1968; Kirk-Othmer 1995) have been published and describe various theories proposed on crystal growth. Mixed crystals obtained after the decopperization of the CBS could be considered for separating copper and nickel by solvent extraction.

*Solvent extraction:* This is another commonly used method that is often in vogue in the copper industry; about 20% of the world copper production is done by this process annually from the lean grade ores/waste streams. Copper was recovered from a variety of solid wastes and other lean grade ores by ammonia leaching, solvent extraction with LIX 84, and electrowinning of metal from the stripped solution (Majima et al. 1993; Nigo et al. 1993). Ritcey et al. (1982) studied the solvent extraction separation of copper and zinc from chloride liquors using Acorga P5300 for copper and TBP for zinc. PT-5050 is one of the Acorga products having the advantages of strong extraction, good stripping, and high selectivity for copper (Kirk-Othmer 1995; Majima et al. 1993). Recovery of copper from hydrochloric acid solution and its transfer into  $\text{H}_2\text{SO}_4$  solution were reported using extractant mixtures such as trioctylamine-LIX 54 (Nigo et al. 1993) and Alamine336-LIX 54 (Ritcey et al. 1982; Kordosky 1992; Barakat and Mahmoud 1999).

*Electrowinning (EW):* Thus, copper and nickel separated by solvent extraction as sulphates were subjected to electrowinning to produce copper powder. Electrorefining, EW, and electrodeposition (Calusaru 1979; Walker and Sandford 1979) processes have been used mostly to recover pure copper powder for powder metallurgical (P/M) applications due to various useful properties such as dendritic structure, variable apparent densities, etc. These properties of metal powder deposited on the cathode depend on various parameters such as concentration of ions, pH, bath temperature, current density, presence of additives in

the electrolyte etc. A number of studies have been reported on EW of copper (Price and Davenport 1980, 1981; Pavlovic et al. 2000a; Fabian et al. 2003) from their sulphate solutions. Fabian et al. (2003) studied the crystallite size of electrodeposited copper in detail.

*Hydrogen reduction:* Another route for the preparation of metal powder could be direct hydrogen reduction of aqueous metal salts at elevated temperature and pressure in an autoclave. Metal recovery from the leach liquors of ores/concentrates has been reported by several investigators (Forward and Halpern 1957; Togashi and Nagai 1983; Wodka et al. 1999; Pandey et al. 2000; Shibata et al. 1987; Schavfelberger 1956). Work has also been reported on metal recovery under pressure in the absence of nucleating agent from the acidic and ammoniacal solutions (Volotinen and Taskinen 1991; Mc Cormick 1958; Togashi and Nagai 1983; Ipatiev and Teodovovich 1931; Peters and Von Hann 1964; Macgregor and Halpern 1958). This article gives the overall flavor of the process options opted for the recovery of copper salt or copper powder by different routes. Although some data have been published elsewhere, properties of the products obtained by various routes are stressed in this article. The products obtained were characterized with respect to their physical and chemical properties.

## 2. EXPERIMENTAL

The process options mentioned previously for the recovery of copper as salt and pure powder from the CBS of an Indian copper smelter are detailed here. The copper bleed solution obtained from an Indian copper smelter contains 39.86 g/L Cu, 9.58 g/L Ni, 0.26 g/L Fe, 0.108 g/L Bi, 0.007 g/L As, 0.055 g/L Sb, and 198.04 g/L H<sub>2</sub>SO<sub>4</sub>. To optimize the experimental conditions a model solution containing (g/L) 38.42 Cu, 19.37 Ni, 171.5 H<sub>2</sub>SO<sub>4</sub> was prepared and was used for all the studies.

In the first approach, CBS was evaporated and crystallized to give copper sulphate and mixed copper–nickel sulphate. Bench-scale studies were performed using the model solution with the chemical composition as mentioned previously. Experiments were also carried out by taking the actual CBS procured from I.C.C., Ghatsila, India (with the chemical composition mentioned earlier). A known amount of CBS (600 mL) was taken in a beaker and was heated for different time intervals to attain a definite level of evaporation and was cooled overnight at room temperature. The crystals formed were removed from the mother liquor

and washed with distilled water. Chemical analysis was performed for the mother liquor, wash liquor, and the crystals for metals and acid contents. The crystals were dried in an oven at 40°C and cooled in desiccators and weighed. The copper sulphate recovered during the evaporation and crystallization process could be recycled back into the system, to make up the balance copper level in the electrolytic cell and subsequent metal recovery. The mother liquor with most of the nickel and acid could be used to recover acid for reuse and nickel as salt (Agrawal et al. 1996; Nyirenda 1998).

In the second approach, the partial decopperization of the copper bleed solution was carried out in an EW cell using titanium as the cathode and Pb 6% Sb as the anode. A 1-L CBS was taken in a lead-lined cell and a current density of 100 A/m<sup>2</sup> was applied to deposit the metal at the cathode for a specified time to reduce copper concentration in the CBS equivalent to the concentration of nickel. The purity of deposited copper metal was also determined by chemical analysis. This partially decopperized bleed solution, containing equal amounts of copper and nickel, was subjected to evaporation in the single and two stages to crystallize mixed crystal of copper–nickel sulphate (Kumari et al. 2006). The crystals obtained in the second stage of crystallization were washed with water and dissolved (Table 1). The solution was neutralized with NaOH to

Table 1. Partial decopperization of model and actual CBS

Components	Synthetic CBS: 38.42 Cu, 19.37 Ni, 171.5 H <sub>2</sub> SO <sub>4</sub> , Volume: 1 L	Actual CBS: 39.86 Cu, 9.58 Ni, 0.255 Fe, 0.108 Bi, 0.0007 As, 0.055 Sb, 194.0 H <sub>2</sub> SO <sub>4</sub>
Feed solution Cu (g/L)	38.42	39.85
Cu after EW (g/L)	17.65	9.64
Average voltage (V)	1.92	1.90
Average current (A)	1.28	1.30
Current efficiency (%)	98.33	98.62
Energy consumption (kWh/kg)	1.646	1.660
Deposit character	Sheet	Bright sheet with nodular deposit along edges
Purity (%)	99.87	99.86 Cu, 0.0017 Ni, 0.13 Bi, n.f. Fe and Sb

Volume of CBS: 1 L, Cathode: titanium, Anode: Pb-6% Sb, Number of cathodes: 1, Current density: 100 A/m<sup>2</sup>.

raise the pH to 3.5–4.0, aerated for 24 h to precipitate iron as hydroxide, and filtered. The filtrate so obtained was subjected to solvent extraction using LIX 84 to separate copper from nickel (Agrawal et al. 2002). The loaded copper was stripped with  $\text{H}_2\text{SO}_4$  and was electrolyzed to give pure metal powder.

Electrolysis was carried out on the bench scale with the copper pregnant solution (1 L), comprised of 38.76 g/L Cu and 50 g/L  $\text{H}_2\text{SO}_4$ , at the current density in the range 600–1000  $\text{A}/\text{m}^2$ , the average current in the range 7–12 A, and the average voltage 3–4 V to generate high current efficiency and possibly low energy consumption. The parameters established were substantiated by copper powder synthesis on a large scale (Agrawal et al. 2007). Copper powder recovered was washed with sodium carbonate to neutralize the acid and again was finally treated with a reducing agent to avoid oxidation. The properties of this copper powder were evaluated for P/M application, particularly its chemical composition, size analysis, compressibility, and green density. The powder was annealed at  $\cong 973$  K under a hydrogen environment for 1 h with a soaking time of 30 min in an electrically heated tubular furnace. Flow rate of the  $\text{H}_2$  gas was maintained at 10 L/m. The sample was allowed to cool for about 5 h and was then taken out of the furnace and used for properties evaluation. For hydrogen loss, a known amount of powder was taken in a silica boat and inserted in the tubular furnace. The hydrogen loss was determined by weight loss of the powder at 1148 K for a period of 30 min.

The third option followed to produce pure copper powder from the CBS was a direct hydrogen reduction of the CBS under hydrogen atmosphere at high temperature and pressure. Bench-scale experiments were carried out in a 1-L-capacity autoclave (PARR, Moline, Illinois, USA), which can be operated up to 80 bar pressure and 300°C temperature and the parameters optimized were substantiated with the large-scale experiments (20-L autoclave). The details of this study have been presented elsewhere (Agrawal et al. 2007). Thus, the powder obtained was properly washed with distilled water and treated as described previously. It was further dried at 100°C and stored in a desiccator and analyzed for its purity and other properties.

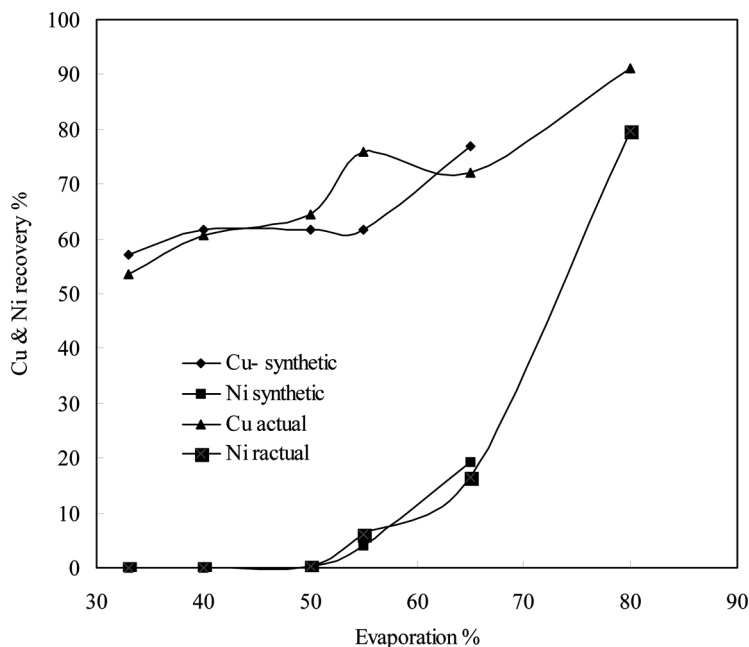
### 3. RESULTS AND DISCUSSION

In order to recover the metallic values from the bleed solution of a copper smelting plant, the following approaches can be followed.



As discussed in our previous article (Kumari et al. 2006), crystallization of a salt depends on the super saturation of the solution. Hence, the CBS was evaporated for a different time period to get different saturation percentages. It was found that with the increase in evaporation from 33% to 65%, the recovery of copper as crystal also increases from 57% to 76.9%. Analysis of these crystals at different evaporation percentages shows an increase in nickel concentration from 0.03% to 19.30% (Figure 1). It was found that Ni does not have much effect up to 55% evaporation, but with the further increase in the evaporation upto 80%, nickel content in the crystal increased sharply making the product (mixed crystal) unsuitable for recycling back into the system. Similar studies were performed with actual CBS.

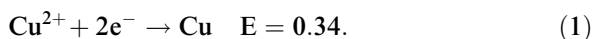
The acid recovered during the crystallization of both solutions was also analyzed for the acid losses and the metal ions left. It was observed that almost total acid remains in the mother liquor at different levels of



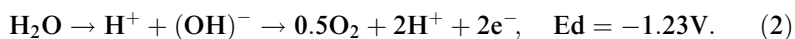
**Figure 1.** Effect of evaporation on the recovery of Cu and Ni from model CBS (g/L): 38.42 Cu, 19.37 Ni, 0.755 Fe, 0.20 Bi, 171.5 H<sub>2</sub>SO<sub>4</sub>, and CBS of ICC (Ghatsila, India) (g/L): 39.86 Cu, 9.58 Ni, 0.255 Fe, 0.108 Bi, 0.055 Sb, 194.0 H<sub>2</sub>SO<sub>4</sub>.

evaporations. Only a small quantity of acid is lost due to evaporation and entrapment in the metal salt, which could be washed with water. At 80% evaporation of the CBS from I.C.C. (Ghatsila, India), the recovery of acid was 83.6%, which may be due to incomplete washing of the crystal.

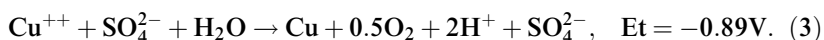
In the second option mentioned, the CBS was subjected to decopperization–crystallization/solvent extraction/EW subsequently. Decopperization at low current density removes pure copper from the bleed stream (Shibayama 1990; Ritcey and Ashbrook 1979) by the following chemical reaction:



The anode reaction is accompanied by the formation of  $\text{O}_2$  gas, which is possible, by imparting a voltage known as decomposition potential ( $E_d$ ) across the electrodes.



The overall reaction is



Thus, the concentration of copper ion in the synthetic solution was reduced from 38.42 g/L to 17.65 g/L on the bench scale, which is equivalent to the level of nickel in the synthetic CBS. While carrying out the decopperization with actual CBS from an Indian copper smelter, the concentration of copper is reduced from 39.85 g/L to about 9.64 g/L, equivalent to nickel in that solution; other conditions remained the same as that for synthetic solution. Good copper sheet deposit was obtained in the copper concentration ranging from 38.42 g/L to 17.65 g/L at a current density of 100 A/m<sup>2</sup> and room temperature. The current efficiency and energy consumption for the deposition were 98.33 and 98.62% and 1.646 and 1.660 kWh/kg for model and the actual CBS from a copper smelter, respectively. The purity of deposited copper cathode was found to be 99.87 and 99.86%. The analysis of cathode copper showed the presence of 0.0048% Ni, 0.13% Bi, and 0.0004% Fe in the deposited metal for synthetic CBS (Table 1).

After the decopperization of the synthetic CBS, the solution obtained was left with 17.65 g/L Cu, 21.18 g/L Ni, and 205.8 g/L sulphuric acid. This solution was further crystallized in single and two stages to see the possibility of getting the mixed crystals. The crystals

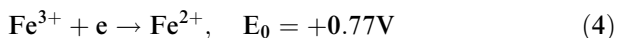
**Table 2.** Effect of evaporation on crystal formation from partially decopperized solution (PDS)

Exemption	Evaporation (%)	Amount of crystal (g)	Analysis of crystal (%)			Recovery in crystal (%)		
			Cu	Ni	H <sub>2</sub> SO <sub>4</sub>	Cu	Ni	H <sub>2</sub> SO <sub>4</sub>
1	First stage 70%	33.28	21.72	2.3	7.66	44.52	3.91	1.35
	Second stage 12%	79.34	8.39	13.67	20.84	68.55	65.82	8.76
2	80%	104.48	12.13	13.48	15.03	74.21	72.69	8.04

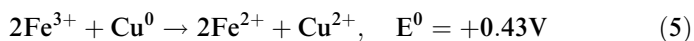
Decopperized CBS [analysis (g/L)]: 17.65 Cu, 21.18 Ni, 205.8 H<sub>2</sub>SO<sub>4</sub>, Volume 920 mL (exemption number 1): 17.96 Cu, 20.39 Ni, 205.8 H<sub>2</sub>SO<sub>4</sub>, volume: 950 mL (exemption number 2)

obtained in a single step were found to be suitable for recycling back to the system and, in a two-stage crystallization, the mixed crystals obtained in the first stage contained appreciable amount of copper, indicating that copper is crystallized before nickel and that it can further be used for making powder or can be recycled for copper makeup in the refinery. This was mainly due to the solubility factor of different metal sulphates and this approach is already exploited in several refineries to recover copper to makeup metal concentration in the electrolyte (Mersmann et al. 1994). In the second stage of crystallization, mixed metal sulphates containing high nickel and low copper were obtained (Table 2), which were leached in water to give the aqueous solution with a composition of 9.53 g/L Cu, 12.81 g/L Ni, 0.5 g/L Fe, and 20 g/L H<sub>2</sub>SO<sub>4</sub>. A detailed study on crystallization is presented elsewhere (Kumari et al. 2006). This solution was then subjected to solvent extraction to separate copper and nickel as sulphates.

The chemical composition of the leach liquor shows that it contains about 0.5 g/L of Fe and our previous experience shows that iron(III) gets extracted along with copper during the solvent extraction process and that it is transferred back to the electrolyte during stripping. This solution on electrolysis decreases the cathode current efficiency leading to high energy consumption and low metal-production rates. The low current efficiency is due to the consumption of a part of the cathode current to reduce ferric iron to a ferrous state, which is depicted by



The ferrous ion thus formed is reoxidized to ferric ion by air or oxygen evolved at anode resulting in a redox reaction. In addition, ferric iron also causes corrosion of cathode loops at the solution line by the reaction



Hence, iron removal from the electrolyte is essential to lower energy consumption and increase the production rate. Thus, the leach solution obtained as described previously containing  $\cong 0.5$  g/L Fe was treated with an NaOH solution with constant stirring to raise the pH of the solution from 1.12 to 3.42 and it was aerated for a period of 24 h at room temperature to precipitate iron as ferric hydroxide, thereby bringing down the iron content from 0.522 to 0.0041 g/L. The time for iron precipitation could be brought down to 6–8 h by increasing the temperature to 80°C. The iron-free solution was subjected to solvent extraction using LIX 84 to separate copper from nickel. Various parameters were optimized on the bench scale and in continuous operation for the separation of copper from nickel; the results are discussed elsewhere (Agrawal et al. 2002). Countercurrent extraction of copper with LIX84 at an A:O ratio of 1:1 and 1:1.5 were simulated and it was found that at O/A of 1/1.5 only 0.0004 g/L copper remained in the raffinate whereas at the A:O ratio of 1:1, 0.434 g/L Cu remains unextracted. Based on these studies, the stages fixed in the mixer settler units were: four stages for extraction, two stages for scrubbing, and two stages for stripping. Data on countercurrent extraction of copper in mixer settler unit with 25% LIX 84 in kerosene are given in Table 3. The composition of raffinate, scrubbed solution, and stripped solution showed the performance of the circuit. The stripped solution is rich in copper and could be used directly for producing copper powder.

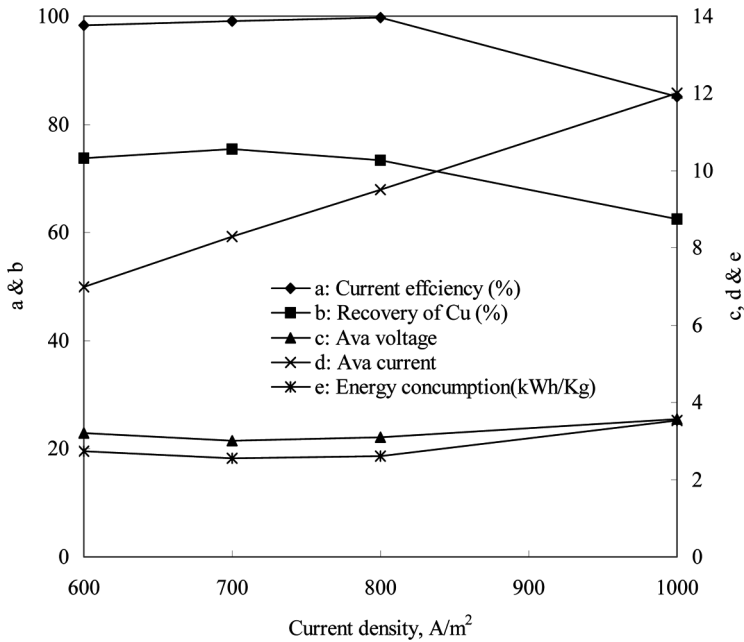
After the separation of copper and nickel as sulphate solutions by solvent extraction, an attempt was taken to produce pure copper powder by electrolysis. Thus, different sets of the experiments were carried out for the recovery of the metal as powder by electrolysis on both the bench and large scales.

Figure 2 shows the results of the experiments on bench scale at various intervals of time at the current density of 600–1000 A/m<sup>2</sup>. At the current density of 700 A/m<sup>2</sup>, the lowest energy consumption of 2.55 kWh/kg with 99.05% current efficiency was noticed and the yield of the copper recovery from electrolysis was 75.46%. Up to the current

**Table 3.** Composition of raffinate, scrub, and strip solution after the separation of Cu and Ni in a mixer settler unit

Operation (number of stages)	Inlet solution (chemical composition/ experimental parameters)	Outlet solution (composition)
Extraction (four stages)	Aqueous feed (g/L): Cu 9.53, Ni 12.81, Flow rate 3.17 L/h, pH 3.06	Raffinate (g/L): Cu 0.001, Ni 11.37, Flow rate 3.171 L/h, pH 2.7
Scrubbing (two stages)	Scrub solution: H <sub>2</sub> SO <sub>4</sub> 1.76 g/L, Flow rate 4.521 L/h	Scrubbed solution (g/L): Cu 0.036, Ni 0.25, Flow rate 4.521 L/h
Stripping (two stages)	Stripping solution: Cu 30.25 g/L, Ni 0.203 g/L, H <sub>2</sub> SO <sub>4</sub> 179.34 g/L, Flow rate 4.521 L/h	Stripped solution: Cu 37.75 g/L, Ni 0.57 g/L, Flow rate 4.521 L/h

Organic feed: 25% I LIX 84, (1.27 g/L Cu, 0.3 g/L Ni, Flow rate 5.04 L/h).



**Figure 2.** Bench-scale experiments at different current densities: Cu 38.76 g/L, H<sub>2</sub>SO<sub>4</sub> 50 g/L, V 1.01 L, cathode: Ti sheet (19.4 × 7.7 × 0.2) cm, anode: Pb-Sb (6%) – 18.8 × 7.4 × 0.4 cm.

density  $800 \text{ A/m}^2$ , the current efficiency is almost the same. At a still higher current density of  $1000 \text{ A/m}^2$ , current efficiency falls to 85%.

The electrolytic method of producing powder allows high-purity products that can well be pressed and sintered. Besides, in recent years it has been shown that by varying the conditions of electrolysis it is possible to not only obtain powders with a wide range of properties but to predict the decisive characteristic of powders, which are of vital importance for the powder quality and for the appropriate purpose (Popov and Pavlovic 1993). For metal powder application, a series of their properties are of interest; size and shape of the particles, bulk weight, flow rate, corrosion resistance, specific surface area, apparent density, and quality of the sintered products. Finally, the properties mentioned depend on the shape and size of the particles, which are influenced by electrolysis conditions (Popov and Pavlovic 1993; Pavlovic et al. 1998; MPIF 06 std 1983). It is necessary to control the following variables to produce electrolytic powder within a specified range of physical properties. These are: 1) electrolyte composition (acid and copper content); 2) electrolyte temperature; 3) electrolyte circulation rate; 4) current density; 5) size and type of anode and cathode; 6) electrode spacing; and 7) time of powder removal. The variables mentioned have strong effects on apparent density; thus, under the conditions optimized for the copper powder produced on the bench scale was characterised for its chemical, physical, and morphological nature.

The purity of the copper powder is found on the basis of chemical analysis and was found to be 99.93%. However, to check the complete purity of the copper powder, acid insoluble (MPIF Standard 06) was determined by heating the copper residue in the muffle furnace at a temperature of 1255 K. The acid insoluble found was 0.046%.

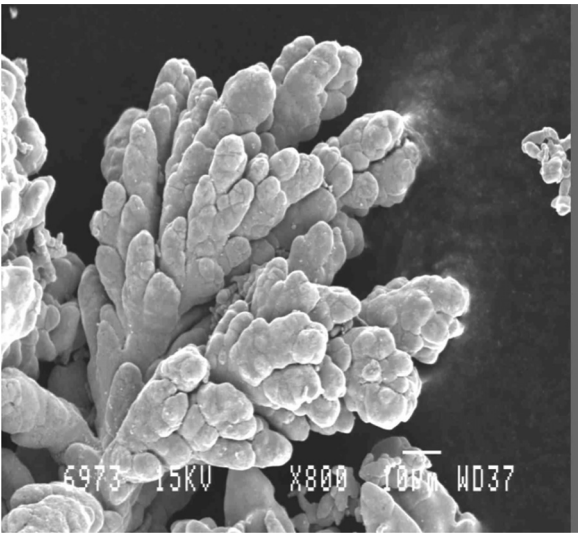
Size analysis of the copper powder (Table 4) indicates that the maximum amount (40.9%) of copper powder is below  $45 \mu\text{m}$ ; the coarser powder, in the particle size range of  $251\text{--}151 \mu\text{m}$ , is about 20%.

The shape of the particle produced has an influential role to play in the determination of powder properties such as apparent density, green strength, compaction, etc. Thus, depending on the production process and the nature of the metal, different shaped particles (granules) can be obtained. Shape is identified through direct, naked-eye, magnifying glass, optical, or electron scanning microscope observation, according to particle size. Thus, scanning electron microscope (SEM) analysis of the copper powder (Figure 3) showed a dendritic nature with the size

**Table 4.** Properties and size analysis of the copper powder produced by electrolysis on bench scale

Physical properties	
Acid insoluble (%)	0.046
Apparent density (g/cc)	0.881
Analysis of the copper powder (%)	0.005 Fe, Pb 0.01474, Ni-NF, Co-NF, Bi-NF, Sb-NF
Purity (%)	99.93
Size analysis of the copper powder produced by electrolysis on bench scale	
Particle size (µm)	Percentage by weight
251	13.59
251–152	7.05
152–104	12.52
104–76	10.03
76–45	15.06
<45	40.86

Current density: 700 A/m<sup>2</sup>, current efficiency: 99.05%, energy consumption: .55 kWh/kg.



**Figure 3.** Electrolytic Cu powder on a bench scale.

of less than 10  $\mu\text{m}$  and with well-developed primary and secondary dendrite arms with the angles between them typical for the face-centered cubic crystals.

Apparent density is one of the decisive characteristics of powders produced. It is represented by the ratio between the mass and the volume of the powder and is measured by letting the powder drop freely through a funnel to fill a 25-cm<sup>3</sup> cylindrical container (ASTM B21247). The apparent density was found to be 0.881 g/cc (Table 4), indicating that the powder formed is very fine in size. This observation can be substantiated by the work of Despi and Popov (1972) and Pavlovic et al. (2000). According to these authors, the powder particles from the same fractions of different powders occupy approximately the same volume, but with a considerably different structure of metallic copper there is a difference in the apparent densities of copper powders obtained under different conditions, depending on the structure of electrodeposits. Obviously,

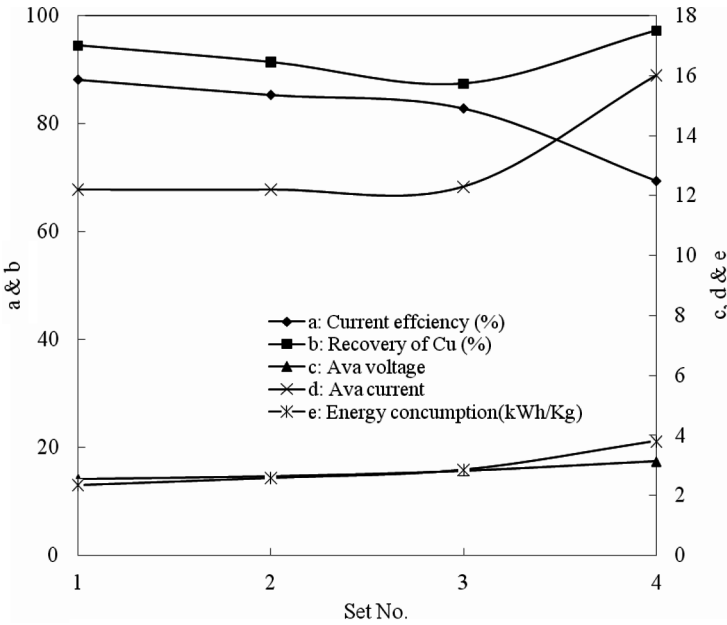
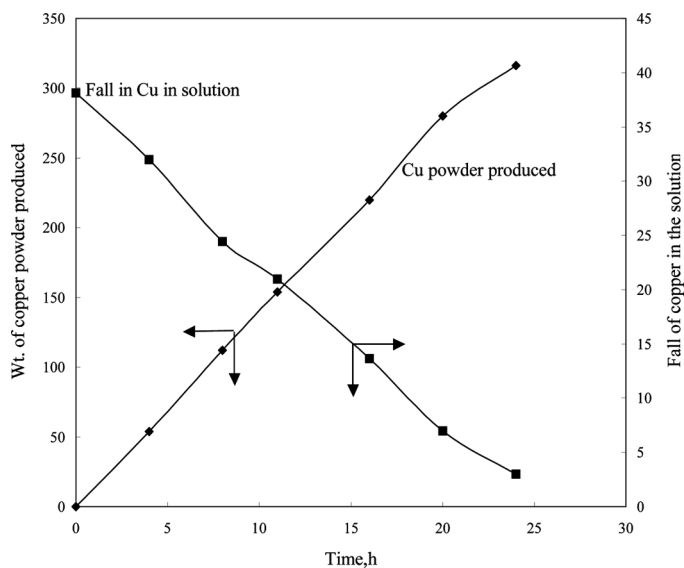


Figure 4. Large-scale preparation of the copper powder by electrolysis, 38.13 Cu, 166.0 H<sub>2</sub>SO<sub>4</sub>, V: 9.0 L, cylindrical rod (stainless steel): 29.9(l)' 2.5(d) 2 numbers, anode: Pb-Sb: Sb (6%) 18(l) 15.4(b) 0.4(t) cm (2Nos).





**Figure 5.** Electrolytic recovery of Cu powder at different time intervals. Current density:  $700 \text{ A/m}^2$ , average voltage: 2.53 V, average current: 12.20 A.

the more dendritic the structure of powder particles, the smaller the apparent density of copper powder.

After the parameters' optimization on the bench scale, four sets of large-scale (9-L solution) experiments were conducted with 1–3 sets at  $700 \text{ A/m}^2$  and a fourth set at  $900 \text{ A/m}^2$  current density. In the experiments at the current density of  $700 \text{ A/m}^2$  for sets 2 and 3 (Figure 4), the current efficiency is nearly the same, i.e., 85 and 88%, and third one (set 1) shows a current efficiency of 82.8%. Energy is found to be low with 2.58 and  $2.34 \text{ kWh/kg}$  for sets 2 and 3 of the experiments. Maximum recovery is achieved in set 4 with 97.22% of copper as powder. On the other hand, current efficiency falls to 69% (set 4) at the current density of  $900 \text{ A/m}^2$ . Annealing of the powder was carried out in the electric furnace at a temperature of  $973 \pm 2 \text{ K}$  for 1 h under a reducing atmosphere of  $\text{H}_2$  gas. The  $\text{H}_2$  gas flow has been controlled to 10 L/min. Thus, the copper powder produced was annealed and the properties examined before and after annealing are mentioned in Table 5.

Chemical analysis of the annealed copper powder shows its purity as 99.95%. The hydrogen loss for the annealed sample is found to be 0.72%.

**Table 5.** Properties and size analysis of copper powder produced by electrolysis on a large scale

Parameters	Electrolytic Cu produced on a large scale	Typical properties of Cu powder by electrolysis*
Acid insoluble (%)	Annealed 0.27% Unannealed 0.12%	0.03% maximum
Apparent density (g/cc)	Annealed 3.04 g/cc Unannealed 2.9 g/cc	1.5–4
Hydrogen loss (%)	0.72 (annealed powder)	0.1–0.75
Chemical analysis of the copper powder (%)	0.0072 Fe, Ni-NF, Co-NF, 0.0025 Pb, 0.0071 Bi, 0.037 Sb (annealed powder)	—
Purity (%)	99.95 (annealed powder)	99.0–99.5
Size range (µm)	Weight of the powder (%) (A)	<45 µm: 5–90%
500–300	11.8	
300–250	5.0	
250–150	12.4	
150–100	11.4	
100–0.2	46.2	
Green density (g/cm <sup>3</sup> )		
(Unsieved) (<152 µm)	8.70	—
(<152 µm)	8.66	
(< 104 µm)	8.74	

Conditions: current density: 700 A/m<sup>2</sup>, average voltage: 2.53 V, average current: 12.20 A  
NF: Not found, A: annealed, UA: unannealed.  
\*Taubenbiat (1974).

An increase in the acid insolubility of the powder after annealing was found to be 0.27% as compared to a value of 0.12% before annealing.

Apparent density (ASTM B212) of the copper powder (sample 2) was found to be 2.9 g/cc before annealing and after annealing it rose to 3.04 g/cc. There is a variation in the apparent density of the Cu powder produced at bench and larger scales. This may be due to several factors such as variation in size and shape of the electrodes, the distance between the electrodes, etc. Moreover, the powder so formed was not removed immediately after the electrolysis. All these factors are responsible for the variation in the apparent density of the copper powder produced on bench and large scales.

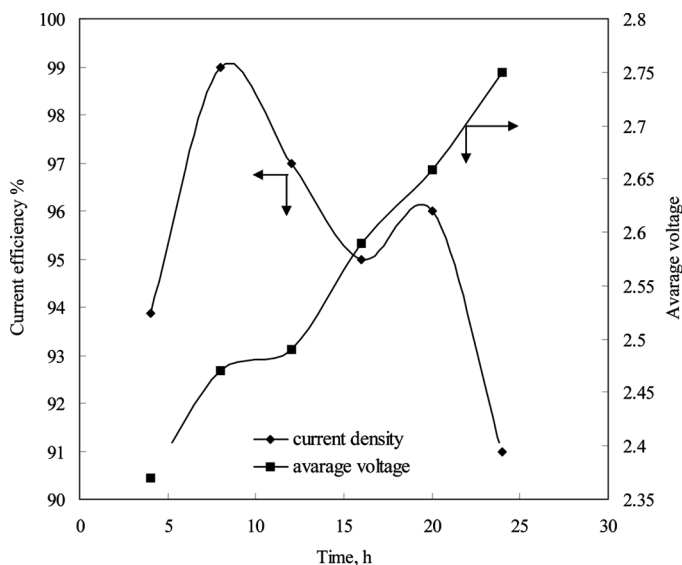
Size analysis of annealed and unannealed copper powder is determined in the Shimadzu centrifugal size analyser (Table 5). The maximum

amount of powder is below  $150\text{ }\mu\text{m}$ ; the annealed powder is finer than unannealed sample.

The green density (MPIF 45 1951) and compactibility (MPIF 15 1951) of the copper powder is determined by taking a calculated amount of the copper powder in a die of the cross-sectional area ( $\pi/4d^2$ )  $\text{inch}^2$  under the applied load of 8 tons. The required load is 30 tsi where  $d$  is diameter of the die (1.5 cm). Thus, the cross-sectional area of the die was calculated as  $1.766\text{ cm}^2 = 0.2738\text{ in}^2$ . Green density ( $D\text{ g/cm}^3$ ) of the compact is given as  $1273 * W/d^2 * h$  where  $W$  is the mass of the test cylinder in millimeters,  $d$  is the diameter of the test cylinder in millimeters, and  $h$  is the height of the test cylinder in millimeters.

The density was found to be  $8.74\text{ g/cc}$  for the annealed powder of the  $<104\text{-}\mu\text{m}$  size, which is close to the known value. The green density of the unsieved powder  $<152\text{-}\mu\text{m}$  size is nearly the same (Table 5).

The rate of copper powder produced by electrolysis on a large scale, as presented in Figure 5, shows a linear increase in the production of copper with the fall of metal in the aqueous phase. The current efficiency was 99% in 8 h with energy consumption of  $2.23\text{ kWh/kg}$



**Figure 6.** A plot between current efficiency and average voltage versus time for the preparation of copper powder on a large scale. Current density:  $700\text{ A/m}^2$ , average voltage:  $2.53\text{ V}$ , average current:  $12.20\text{ A}$ .

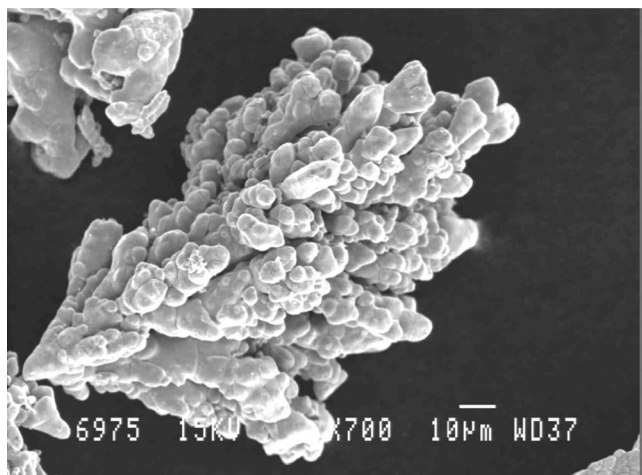


Figure 7. Electrolytic copper powder produced on a large scale.

(Figure 6). This figure also infers a gradual increase in average voltage with time.

SEM pictures of annealed copper powder produced at  $700 \text{ A/m}^2$  are represented in Figure 7, which show that copper powder was found to be dendritic in nature, having the advantage of better compaction for P/M application. If we compare these properties with the typical properties of Cu powder by electrolysis (Table 5), we find that the powder produced has the comparable properties and is suitable for powder metallurgical components in the electronic and electrical industries where high electrical and thermal conductivities are required. However, it is suitable for most other P/M applications as well.

### 3.1. Copper Powder from CBS by Direct Hydrogen Reduction

Bench-scale experiments for optimizing the parameters for the recovery of copper powder by hydrogen reduction of the copper bleed solution were performed under different conditions. A model solution containing  $40.0 \text{ g/L}$  Cu and  $10.43 \text{ g/L}$  Ni as major metallic values along with  $194 \text{ g/L}$   $\text{H}_2\text{SO}_4$  was used for these studies; details of this study are reported elsewhere (Agrawal et al. 2006).

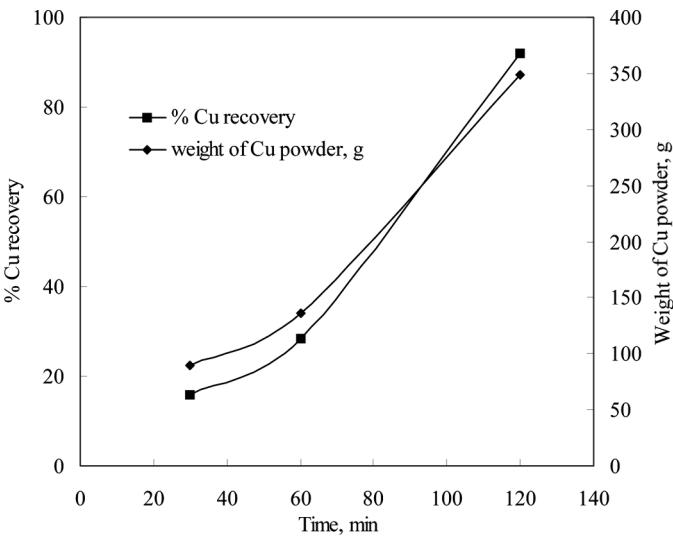
Copper powder formed in each experiment was filtered and washed as reported earlier. The purity of the copper powder produced under

**Table 6.** Chemical analysis of copper powder produced by hydrogen reduction under various experimental conditions on bench scale

Parameters	Constituents (%)
Temperature 453 K, p 20 kg/cm <sup>2</sup> Reduction time 1 h	Ni-NF, Fe 0.0058, Bi-NF, Sb 0.0028, purity 99.99
Temperature 423 K, p 20 kg/cm <sup>2</sup> , Reduction time 2 h	Ni-NF, Fe-NF, Bi-NF, Sb 0.0039, purity 99.99
Temperature 453 K, p 20 kg/cm <sup>2</sup> Reduction time 2 h, Fe dosage 750 ppm	Ni-NF, Fe 0.0021, Bi 0.0229, Sb 0.0022, purity 99.97
Temperature 453 K, p 20 kg/cm <sup>2</sup> Reduction time 2 h, Fe dosage 500 ppm	Ni-NF, Fe-NF, Bi-NF, Sb 0.0027, purity 99.99

40.0 g/L Cu, 10.43 g/L, and 194 g/L H<sub>2</sub>SO<sub>4</sub>, rpm of stirrer: 400.

different conditions on bench scale is given in Table 6. The parameters optimized on the bench scale were substantiated by a large-scale copper powder production in a 20-L autoclave with model and actual CBS. The parameters studied in different sets are given in Figure 8. After treating



**Figure 8.** Effect of time on Cu powder recovery by hydrogen reduction. Cu powder as seed 50 g, p 20 kg/cm<sup>2</sup>.

the copper powder formed as discussed previously, it was dried and stored for properties evaluation. Properties of the copper powder have been studied after annealing at 973 K under the hydrogen gas flow of 10.5 L/min for 1 h. The annealed powder from model and actual CBS was examined for various properties such as apparent density, acid

**Table 7.** Properties and particle size analysis of annealed copper powder produced on a large scale (20-L autoclave) by hydrogen reduction from model and actual CBS

Parameters	Experimental conditions: Cu powder as seed: 25 g, P applied, 24 kg/cm <sup>2</sup> , temperature 453 K, time of reduction 120 min	
	Model CBS analysis (g/L): Cu 38.42, Ni 19.37, Bi 0.11, Fe 0.26, H <sub>2</sub> SO <sub>4</sub> 171.5	Actual CBS analysis (g/L): Cu 39.85, Ni 9.58, Bi 0.11, Fe 0.26, H <sub>2</sub> SO <sub>4</sub> 194.04
Weight of powder obtained, g	335.4	350.8
Recovery %	95	99.4
Nature of powder obtained	Lustrous copper powder	
Properties of the annealed copper powder produced from model and actual solution		
Apparent density (g/cc)	3.50	3.49
Flow rate (sec/50 g)	35.6	46.0
Hydrogen loss (%)	0.195	0.598
Chemical analysis of the copper powder (%)	Ni: 0.0055, Fe: 0.0046, Bi 0.0082, Sb 0.0022	Ni: 0.0009, Fe 0.0036, Bi NF, Sb NF
Purity (%)	99.785	99.398
Particle size of annealed copper powder (μm)		
212	38.48	29.19
212–150	30.42	30.60
150–106	11.75	11.91
106–75	6.82	6.89
75–63	2.22	2.62
63–45	7.64	7.41
45	2.51	11.28
Weight of Cu powder taken (g)	100.02	100.04
Weight of Cu powder after sieving	99.84	99.90
% weight loss during sieving	0.18	0.14
Green density (g/cm <sup>3</sup> )	8.25	8.57

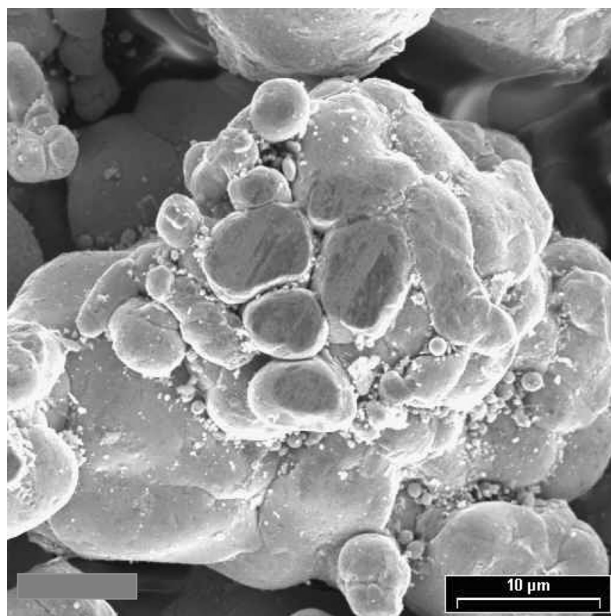


Figure 9. Copper powder produced during a large-scale experiment from the actual bleed stream.

insoluble, purity of the copper powder, flow rate, hydrogen loss. The values are given in Table 7. Size analysis of annealed copper powder produced from model and actual solutions are also given in Table 7. The annealed powder from synthetic and actual solutions had 60–68% size in the range 212–150 μm and 30–40% particles <150 μm in size. SEM of the copper powder (Figure 9) shows the spherical nature of the particles; however, these particles were agglomerated, probably because the powder was not removed immediately after their synthesis. However, it was highly lustrous in appearance.

Compactness and the green density of annealed copper powder were also determined and are given in Table 7. The green density of <104-μm-sized powder from the model solution was found to be 8.57 g/cm<sup>3</sup>, whereas it was 8.57 g/cm<sup>3</sup> for the powder from CBS, irrespective of size. Acid insoluble and H<sub>2</sub> loss suggested that copper powder produced by electrolytic and hydrogen-reduction methods were suitable for P/M applications.

#### 4. CONCLUSION

The CBS from the copper smelter plants contains a high concentration of copper and nickel; therefore, various options have been tried to recycle or reuse it as salts or pure copper powder. Different process routes were investigated viz:

- 1) Evaporation and crystallisation.
- 2) Partial decopperization–crystallization separation of Cu-Ni from the mixed solution by solvent extraction using LIX 84 and preparing electrolytic copper powder by EW.
- 3) Producing copper metal by direct hydrogen reduction.

In the first scheme, about 25% copper sulphate was produced, which could be recycled back to the refinery for metal makeup. It was found that an increase in the percentage evaporation of copper bleed solution from 33 to 65% improved in copper sulphate recovery from 57.1 to 76.9%. The recovery of copper increased from 76.0 to 91.0% with an increase in percentage evaporation from 55 to 80% from the CBS (I.C.C., Ghatshila, India). However, at higher evaporation, i.e., beyond 50%, nickel sulphate also crystallized along with copper sulphate, making it unsuitable for recycling.

In the second scheme, CBS was partially decopperized to a level of 17–18 g/L Cu at a current density of 100 A/m<sup>2</sup>. The decopperized solution was crystallized to get a mixed crystal so formed was washed with distilled water and leached in water with a composition of 9.53 g/L, 12.81 g/L Ni, 0.5 g/L Fe, 20 g/L H<sub>2</sub>SO<sub>4</sub>.

The leach solution was purified for iron removal prior to solvent extraction and was subjected to solvent extraction using LIX 84. Loaded copper was stripped by acid and pure copper powder was prepared by electrolysis of the copper sulphate solution.

Parameters optimized for copper recovery by electrolysis on the bench scale were scaled up to 9.0 L per batch. A 95% copper powder was recovered at a current density of 700 A/m<sup>2</sup>, which was dendritic in nature. Annealed powder had an apparent density of 3.04 g/cc, hydrogen loss of 0.72%, acid insoluble is 0.27%, and green density of 8.7 g/cc. The rate of the metal deposition was almost linear at the current density of 700 A/m<sup>2</sup>; the particle-size range of the annealed powder was 500–5.0 µm with maximum amount (21%) of 20–10 µm in size.



The last scheme endeavors to produce high value copper and nickel powders by aqueous hydrogen reduction of the CBS. Parameters optimized for the bench scale were scaled up to 9.0 L per batch.

Experiments were performed with model and actual CBS. A 99% copper powder recovery was achieved by hydrogen reduction at a pressure of 24 kg/cm<sup>2</sup>, reaction temperature of 180°C, stirring speed of 400 rpm for a reaction time of 2 h. The copper powder thus obtained was lustrous in nature.

After the recovery of copper powder, the mother liquor was further treated to recover nickel values from it.

Thus, CBS with such a high acidity can either be used directly for copper powder recovery by hydrogen reduction or by the electrolytic route after the pretreatment of CBS by decopperization-crystallization solvent extraction. The powders produced by both routes were found to be suitable for P/M applications.

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